Articles

Stereoselective Dihapto-Binding of Prochiral Aromatic Compounds by {TpRe(CO)(PMe$_3$)}: Synthesis, Characterization, Stability, and Enantiofacial Discrimination (Tp = Hydrido(tris)pyrazolylborate)

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Synthetic access to {TpRe(CO)(PMe$_3$)} and the ability of this fragment to bind unsaturated compounds are reported. A variety of complexes of the type TpRe(CO)(PMe$_3$)(η^2-L) (L = cyclohexene, cyclopentene, naphthalene, phenanthrene, thiophene, 2-methylthiophene, furan, or acetone) have been isolated and characterized, and stereochemical and stability issues of aromatic molecules bound to {TpRe(CO)(PMe$_3$)} are discussed in detail. In particular, a solid-state structural study of TpRe(CO)(PMe$_3$)(η^2-cyclohexene) has provided a foundation for a discussion of the stereoelectronic features of the Re(I) fragment, and substitution reactions of an aromatic ligand by acetone provide insight into the stability of these aromatic complexes. In addition, a solid-state X-ray diffraction study of the Re(II) complex TpRe(CO)(PMe$_3$)(OTf) (OTf = trifluoromethanesulfonate) is presented.

Introduction

Given the prevalence of carbocyclic ring systems in nature and compounds of pharmacological interest,[1] the ability to selectively manipulate aromatic substrates is an important synthetic goal. However, due to the inherent stability imparted by aromaticity, the selective dearomatization of this class of compounds is arduous.[2−4] One of the most successful strategies for enhancing the reactivity of arenes has been to coordinate them (η^6) to an electron-deficient transition metal.[5−8] In these systems, the metal promotes nucleophilic addition to the arene as well as deprotonation of the aryl and benzylic protons.

The η^2-binding of an aromatic compound by an electron-rich metal fragment provides complementary reactivity to that encountered with the η^6-bound aromatic systems.[9] In particular, the pentaammineosmium(II) fragment forms stable η^2-bound aromatic complexes with an impressive breadth of substrates and activates the aromatic ligand toward electrophilic addition reactions.[9] A diverse range of regio- and stereocontrolled aromatic derivatization reactions (including dearomatization reactions) has been performed using this osmium fragment.[9] Yet, the use of stoichiometric osmium as a tool in organic synthesis has been largely unrealized owing to the cost of the metal, its toxicity, and the dicationic charge of the complexes which limit the solvent environments and purification techniques available. In addition, the inability to manipulate the ligand set of {Os(NH$_3$)$_5$}$^{2+}$ without disrupting the binding affinity precludes the use of a chiral derivative of the pentaammineosmium system for use in enantioselective reactions.[10,11] Thus, our lab has been targeting the synthesis of π-basic metal systems that mimic the osmium in its ability to dearomatize organic systems, yet overcome the disadvantages mentioned above. Given the paucity of thermally stable η^2-aromatic complexes,[12−23] we have focused our search on complexes

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(1) Corey, E. J.; Cheng, X. *The Logic of Chemical Synthesis*; John Wiley and Sons: New York, 1989.

(2) Mander, L. N. In *On the Birch Reduction*; Trost, B. M., Fleming, I., Eds.; Pergamon Press: Oxford, 1991; Vol. 8, p 489.

(3) Mander, L. N.; Hook, J. M. *Nat. Prod. Rep.* **1986**, 37.

(4) Mander, L. N. *Synlett* **1991**, 134.

(5) Semmelhack, M. F. In *Comprehensive Organic Synthesis*; Trost, B. M., Ed.; Pergamon Press: Oxford, 1990; Vol. 4, Chapter 2.4, p 517.

(6) Pearson, A. J.; Gontcharov, A. V.; Woodgate, P. D. *Tetrahedron Lett.* **1996**, *37*, 3087.

(7) Astruc, D. *Tetrahedron* **1983**, *39*, 4027−4095.

(8) Pearson, A. J.; Bruhn, P. R.; Gouzoules, F.; Lee, S.-H. *J. Chem. Soc., Chem. Commun.* **1989**, 659.

(9) Harman, W. D. *Chem. Rev.* **1997**, *97*, 1953.

(10) Barrera, J.; Orth, S. D.; Harman, W. D. *J. Am. Chem. Soc.* **1992**, *114*, 7316.

(11) Orth, S. D.; Barrera, J.; Rowe, S. M.; Helberg, L. E.; Harman, W. D. *Inorg. Chim. Acta* **1998**, *270*, 337.

(12) For examples of η^2-aromatic complexes, see refs 13−23.

(13) Tagge, C. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 6908.

(14) Jones, W. D.; Feher, F. J. *J. Am. Chem. Soc.* **1982**, *104*, 4240.

(15) Jones, W. D.; Dong, L. *J. Am. Chem. Soc.* **1989**, *111*, 8722.

(16) Boese, R.; Stanger, A.; Stellberg, P.; Shazar, A. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1475.

(17) Sweet, J. R.; Graham, W. A. G. *J. Am. Chem. Soc.* **1983**, *105*, 305.

(18) Sweet, J. R.; Graham, W. A. G. *Organometallics* **1983**, *2*, 135.

(19) Agbossou, S. K.; Bodner, G. S.; Patton, A. T.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1184.

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that are isoelectronic with $\{[Os(NH_3)_5]^{2+}\}$.[24] We now wish to report the full details of the synthesis of an asymmetric Re(I) π-base that binds furan, thiophene, phenanthrene, and naphthalene in a dihapto-coordination mode. A portion of this work previously has been communicated.[25] Throughout this article, we will draw extensively upon the comprehensive studies of the structurally related chiral Lewis acids $\{Cp^xRe(NO)(PPh_3)\}^+$ (Cp^x = cyclopentadienyl or pentamethylcyclopentadienyl).[26]

Results

The $\{TpRe(CO)_2\}$ fragment was previously demonstrated to bind naphthalene, furan, and *N*-methylpyrrole in a dihapto-coordination mode.[27] However, the monomeric complexes $\{TpRe(CO)_2(\eta^2\text{-Ar})\}$ (Ar = furan, naphthalene, or *N*-methylpyrrole) were not stable enough to permit isolation, and only $\eta^2{:}\eta^2$-(μ-aromatic)-bridged binuclear complexes were isolated. We reasoned that the presence of two strong π-acidic ligands (carbon monoxide) in the coordination sphere rendered the Re(I) metal center too electron-deficient to form substitution-inert monomeric η^2-aromatic complexes. Replacement of a CO ligand with a more electron-donating moiety would result in a more π-basic metal fragment that could lead to thermally and kinetically stable monomeric complexes with aromatic ligands. After attempts to remove a single CO ligand from complexes of the type $TpRe(CO)_2(L)$ {L = PMe_3 (**1**), $P(OMe)_3$ (**2**), or NH_3 (**3**)} failed to yield synthetically useful results, a new synthetic strategy was formulated[28] involving the stepwise reduction of high-valent rhenium ($NaReO_4$).

The production of $TpRe^V(Cl)_2(O)$ (**4**) from $NaReO_4$, KTp, and HCl has been previously reported.[29,30] The oxo ligand of **4** is electrophilic, and reaction with trimethylphosphine yields $TpRe^{III}(Cl)_2(O{=}PMe_3)$ (**5**) in excellent yield (95%). The lability of the phosphineoxide ligand of **5** in refluxing DME (DME = 1, 2-dimethoxyethane) allows access to $TpRe^{III}(Cl)_2(PMe_3)$ (**6**).[31] Complexes **5** and **6** display resonances in their ^1H NMR spectra that are shifted due to the paramagnetic character of the metal center.[32,33] The proton chemical shifts range from -19 to 13 ppm for compounds **5** and **6**.

To access the desired $\{TpRe(CO)(PMe_3)\}$ fragment, it is necessary to reduce $TpRe^{III}(Cl)_2(PMe_3)$ (**6**) to Re(I) and coordinate carbon monoxide. We have previously reported the synthesis of $TpRe(CO)(PMe_3)(\eta^2\text{-cyclohexene})$ (**7**) from $TpRe^{III}(Cl)_2(PMe_3)$ (**6**), Na/Hg, cyclohexene, and carbon monoxide gas.[25] The earlier reported conditions included the use of a specialized pressure tube apparatus to place the reaction solution under CO (g) pressure (approximately 10 psi), and the production of two dicarbonyl side products ($TpRe(CO)_2(PMe_3)$ (**1**) and $TpRe(CO)_2(\eta^2\text{-cyclohexene})$) was noted.[34] We have now found a more convenient and higher yield route to complex **7** which obviates the need for specialized equipment. The reaction of **6**, 1 atm of CO (g), cyclohexene (20 equiv), and sodium amalgam (approximately 2.4 equiv) in benzene at 60 °C, yields a dark brown solution. Purification via chromatography yields $TpRe(CO)(PMe_3)(\eta^2\text{-cyclohexene})$ (**7**) in 61% yield (Scheme 1). (Table 1 lists characterization information for the series of $TpRe(CO)(PMe_3)(\eta^2\text{-L})$ complexes reported herein.) The corresponding cyclopentene complex (**8**) can be synthesized in an analogous fashion. The dicarbonyl complex $TpRe(CO)_2(PMe_3)$ (**1**) can still be detected by IR and ^1H NMR spectroscopies in these crude products, but the yield of this undesirable product is <10%.

The η^2-olefin complexes **7** and **8** are similar to numerous olefin complexes of the type $[Cp^xRe(NO)(PPh_3)(\eta^2\text{-olefin})]^+$.[26,35−40] However, the $\{TpRe(CO)(PMe_3)\}$ fragment is anticipated to be considerably more electron-rich. The low-energy CO stretching frequency (ν_{CO} = 1796 cm^{-1}, KBr) and $Re^{II/I}$ potential ($E_{1/2}$ = 0.23 V vs NHE) support this notion (cf. for the complex $[Os(NH_3)_5(cyclohexene)]^{2+}$ the d^6/d^5 couple is 0.55 V, NHE).[41] A singlet at -18.1 ppm in the $^{31}P\{^1H\}$ spectrum is typical for $Re^I{-}PMe_3$ phosphine complexes.[42] The ^1H NMR spectrum shows five multiplets which integrate for 2:2:1:3:2 protons for the cyclohexene ligand, and five Tp doublets are an indication of an asymmetric metal center (i.e., all three pyrazolyl rings are inequivalent with two Tp doublets coincidentally overlapping). Two of the Tp triplets are isochronous in acetone-d_6; however, three distinct triplets are observed in CD_2Cl_2. The presence of two high-field chemical shifts for the olefinic carbons in the ^{13}C NMR spectrum (51.2 and 49.1 ppm vs 127.7 ppm for free cyclohexene) is indicative of coordination to an asymmetric and π-basic metal fragment. That is, the olefinic carbons are inequivalent due to binding to the chiral metal center, and the upfield shifts reflect an increase in sp^3 character for the bound carbons.[43,44] The resonance at 49.1 ppm is coupled to phosphine ($^2J_{PC}$ = 10 Hz), and this resonance is assigned

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(20) Evans, W. J.; Ulibarri, T. A.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 219.

(21) Kleckley, T. S.; Bennett, J. L.; Wolczanski, P. T.; Lobkovsky, E. B. *J. Am. Chem. Soc.* **1997**, *119*, 247.

(22) Neithamer, D. R.; Párkányi, L.; Mitchell, J. F.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1988**, *110*, 4421.

(23) Heijden, H. v. d.; Orpen, A. G.; Pasman, P. *J. Chem. Soc., Chem. Commun.* **1985**, 1576.

(24) For examples of our work in this area, see refs 6−11 from ref 27 in this article.

(25) Gunnoe, T. B.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1999**, *121*, 6499.

(26) Gladysz, J. A.; Boone, B. J. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 6, 550.

(27) Gunnoe, T. B.; Sabat, M.; Harman, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 8747.

(28) Photolytic, thermal, and oxidative (Me_3NO) conditions were attempted. In addition, efforts were made to remove a single carbonyl under these conditions at the Re(II) oxidation state.

(29) Abrams, M. J.; Davison, A.; Jones, A. G. *Inorg. Chim. Acta* **1984**, *82*, 125.

(30) Brown, S. N.; Mayer, J. M. *Inorg. Chem.* **1992**, *31*, 4091.

(31) The preparation of **6** is similar to a procedure reported for the synthesis of $TpRe(Cl)_2$(pyridine). Brown, S. N.; Mayer, J. M. *Organometallics* **1995**, *14*, 2951.

(32) Sanders, J. K. M.; Hunter, B. K. *Modern NMR Spectroscopy: A Guide for Chemists*; Oxford University Press: New York, 1993.

(33) Jesson, J. P. *NMR of Paramagnetic Molecules*; Academic Press: New York, 1973.

(34) $TpRe(CO)_2(\eta^2\text{-cyclohexene})$ was identified by comparison to the known complex $TpRe(CO)_2(\eta^2\text{-cyclopentene})$. See ref 27.

(35) Bodner, G. S.; Peng, T.-S.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1990**, *9*, 1191.

(36) Lowalczyk, J. J.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1991**, *124*, 729.

(37) Peng, T.-S.; Gladysz, J. A. *J. Am. Chem. Soc.* **1992**, *114*, 4174.

(38) Pu, J.; Peng, T.-S.; Mayne, C. L.; Arif, A. M.; Gladysz, J. A. *Organometallics* **1993**, *12*, 2686.

(39) Bodner, G. S.; Fernández, J. M.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1988**, *110*, 4082.

(40) Kowalczyk, J. J.; Arif, A. M.; Gladysz, J. A. *Chem. Ber.* **1991**, *124*, 729.

(41) Harman, W. D.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 7906.

(42) Cusanelli, A.; Sutton, D. *Organometallics* **1995**, *14*, 4651.

(43) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: New York, 1981.

(44) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33.

Scheme 1. Synthetic Route to TpRe^{II}(CO)(PMe$_3$)(OTf) (10)

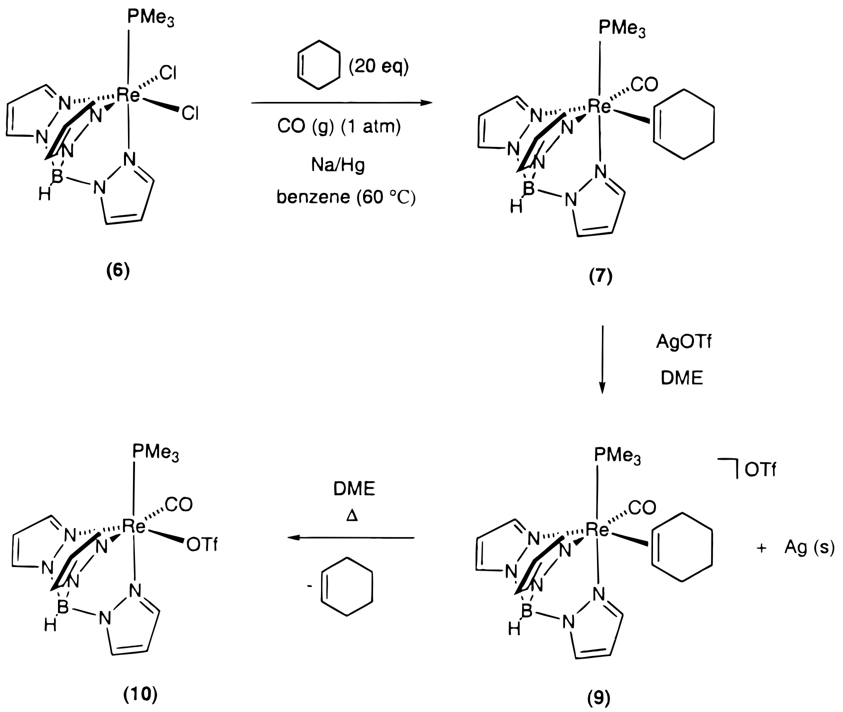

Table 1. Spectroscopic and Electrochemical Data for Complexes 7 and 12−16

complex	ν_{CO}[a] (cm^{-1})	ν_{BH}[a] (cm^{-1})	$E_{1/2}$ (II/I)[b] (V)	^{13}C data for bound carbons[c] (ppm)	^{31}P NMR[d] (ppm)
TpRe(CO)(PMe$_3$)(η^2-cyclohexene) (**7**)	1796	2478	0.23	51.2 and 49.1	−18.1
TpRe(CO)(PMe$_3$)(η^2-naphthalene) (**12**)	1825	2472	0.19	57.4 and 53.1	−23.4
TpRe(CO)(PMe$_3$)(η^2-phenanthrene) (**13**)	1820	2471	0.17	58.0 and 51.4	−19.5
TpRe(CO)(PMe$_3$)(η^2-furan) (**14**)	1826	2478	0.30[d]	48.9 and 102.5[e]	−19.6[e]
TpRe(CO)(PMe$_3$)(η^2-thiophene) (**15**)	1826	2478	0.01	65.0 and 61.0[e]	−22.0[e]
TpRe(CO)(PMe$_3$)(η^2-acetone) (**16**)	1819	2482	0.26[d]	84.2	−11.9
TpRe(CO)(PMe$_3$)(η^2-CpH) (**18**)	1814	2481	0.26[d]	84.2	−19.2

[a] KBr [b] Recorded in DMA (with TBAH electrolyte) vs NHE. [c] Rcorded in CD$_2$Cl$_2$. [d] Referenced vs external phosphoric acid. [d] Reported for $E_{p,a}$. [e] Reported for major diastereomer.

as the bound carbon syn to the phosphine ligand.[35,43] Analogous carbon−phosphorus coupling features were observed for all {TpRe(CO)(PMe$_3$)} complexes reported herein.[45]

Table 2. Selected Crystallographic Data and Collection Parameters for TpRe(CO)(PMe$_3$)(η^2-cyclohexene) (7) and TpRe(CO)(PMe$_3$)(OTf) (10)

	7	10
empirical formula	$C_{19}H_{29}BN_6OPRe$	$C_{14}H_{19}BF_3N_6O_4PSRe$
fw	585.47	652.39
cryst	green prism	green needle
cryst dimens, mm	0.29 × 0.41 × 0.23	0.26 × 0.28 × 0.47
cryst syst	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1/c$ (No. 14)
a, Å	8.582(2)	10.094(4)
b Å	15.443(4)	11.446(4)
c, Å	16.982(3)	19.087(5)
β, deg	97.24(2)	91.24(3)
V, Å^3	2232.7(8)	2204(1)
Z	4	4
D_{calcd}, g cm^{-3}	1.742	1.965
μ(Mo Kα), cm^{-1}	55.39	57.40
temp, °C	−100	−100
2θ max, deg	46.1	46.3
total no. of reflns	3504	3499
no. of unique reflns	3259	3287
R	0.031	0.033
R_w	0.042	0.044

X-ray quality crystals of TpRe(CO)(PMe$_3$)(η^2-cyclohexene) (**7**) were grown by slow solvent evaporation from a toluene/hexanes solution of **7**.[46] Data from the structural study are presented in Table 2, important bond lengths and angles are depicted in Table 3, and an ORTEP diagram of complex **7** is shown in Figure 1. The unsaturated carbon−carbon bond of the olefinic ligand is aligned nearly parallel to the Re−phosphine bond axis (vide infra). Thus, the Re−P−C(1)−C(2) dihedral angle is calculated to be 5.4°. The closely related complex [(η^5-C$_5$H$_4$CH$_3$)Re(NO)(PPh$_3$)(η^2-cyclopentene)][BF$_4$] displays a dihedral angle (8.8°) similar to that of complex **7**.[40] The rhenium−olefin bond distances {Re−C(1) 2.235(8); Re−C(2) 2.193(8)} indicate that the alkene is unsymmetrically bound. The approximately 0.04 Å increase in the bond distance from rhenium to C(2) {cf. Re−C(1)} is likely a reflection of the steric bulk of the trimethylphosphine ligand relative to the trans pyrazolyl ring. The unsymmetrical binding of the olefin ligand is rather dramatic when compared to similar complexes.[35,40] Interestingly, although the phosphine moiety is more sterically cumbersome than the trans pyrazolyl ring, a distance of 1.964 Å between the proton on C(17) of the

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(45) Coupling between phosphorus and the bound carbon anti to the trimethylphosphine ligand was not large enough to be observed (<2 Hz).

(46) The structure of complex **7** has previously been reported in part in communication format. See ref 25.

Table 3. Selected Bond Distances (Å) and Angles (deg) for TpRe(CO)(PMe$_3$)(η^2-cyclohexene) (7)

Re−P	2.401(2)	O−C7	1.177(10)
Re−N1	2.240(7)	C1−C6	1.54(1)
Re−N3	2.164(7)	C2−C3	1.53(1)
Re−N5	2.196(6)	C3−C4	1.53(1)
Re−C1	2.235(8)	C4−C5	1.49(1)
Re−C2	2.193(8)	C5−C6	1.54(1)
Re−C7	1.846(9)		
P−Re−N1	88.9(2)	N5−Re−C1	118.9(3)
P−Re−N3	83.7(2)	N5−Re−C2	81.7(3)
P−Re−N5	159.4(2)	N5−Re−C7	95.4(3)
P−Re−C1	79.4(2)	C1−Re−C2	37.3(3)
P−Re−C2	116.6(2)	C1−Re−C7	93.9(3)
P−Re−C7	92.2(3)	C2−Re−C7	95.2(3)
N1−Re−N3	86.9(2)	Re−P−C8	116.7(4)
N1−Re−N5	82.6(2)	Re−P−C9	122.2(3)
N1−Re−C1	89.1(3)	Re−P−C10	113.5(3)
N1−Re−C2	86.8(3)	Re−C1−C2	69.7(5)
N1−Re−C7	177.0(3)	Re−C1−C6	124.0(6)
N3−Re−N5	77.1(2)	C2−C1−C6	120.9(8)
N3−Re−C1	162.8(3)	Re−C2−C1	72.9(5)
N3−Re−C2	158.5(3)	Re−C2−C3	123.6(5)
N3−Re−C7	90.4(3)	C1−C2−C3	120.9(8)

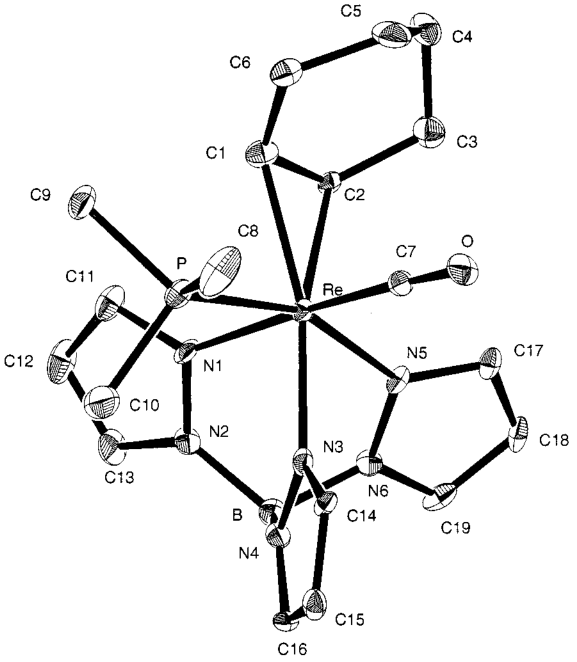

Figure 1. ORTEP diagram of TpRe(CO)(PMe$_3$)(η^2-cyclohexene) (**7**) (30% probability ellipsoids).

Tp and a methylene hydrogen on C(3) of the cyclohexene ligand reflects a steric interaction between the olefinic ligand and the pyrazolyl ring (Figure 1).[47] A discrepancy in the three N−Re−N bond angles is also attributed to this steric interaction. Thus, two of the N−Re−N bond angles are >80° (86.9° and 82.6°), while the N(3)−Re−N(5) bond angle (77.1°) is more acute.

Dissociation of the olefin from **7** or **8** would yield the desired {TpRe(CO)(PMe$_3$)} fragment. However, at the Re(I) oxidation state **7** and **8** proved to be substitution inert even at elevated temperatures. For example, no spectroscopic signs of decomposition were observed upon prolonged heating of the cyclohexene complex **7** in refluxing hexanes (approximately 60 h of reflux). In contrast, upon oxidation to Re(II), the olefin ligands become susceptible to substitution with even weakly coordinating ligands. For example, the reaction of **7** with AgOTf (OTf = trifluoromethanesulfonate) yields a new complex with ν_{CO} = 1912 cm^{-1}, and this new species has been assigned as the simple one-electron oxidation product [TpRe^{II}(CO)(PMe$_3$)(η^2-cyclohexene)][OTf] (**9**) (Scheme 1). After the addition of a small amount of ferrocene to remove excess Ag$^+$ ion and 15 min of refluxing in DME, the CO absorption at 1912 cm^{-1} is replaced by a new absorption at 1866 cm^{-1}, and the new complex is assigned as TpRe(CO)(PMe$_3$)(OTf) (**10**). In addition to its IR spectrum, complex **10** was characterized by cyclic voltammetry, elemental analysis, and a solid-state X-ray structural study (vide infra). The cyclic voltammogram of the triflate complex **10** shows a quasi-reversible reduction wave (II/I) at $E_{1/2}$ = −0.65 V and an irreversible oxidation peak (III/II) at $E_{p,a}$ = 0.87 V (vs NHE). In contrast to the cyclohexene complex **7**, the corresponding [TpRe^{II}(CO)(PMe$_3$)(η^2-cyclopentene)][OTf] (**11**) complex requires several hours of reflux in DME for complete triflate/cyclopentene ligand exchange, and

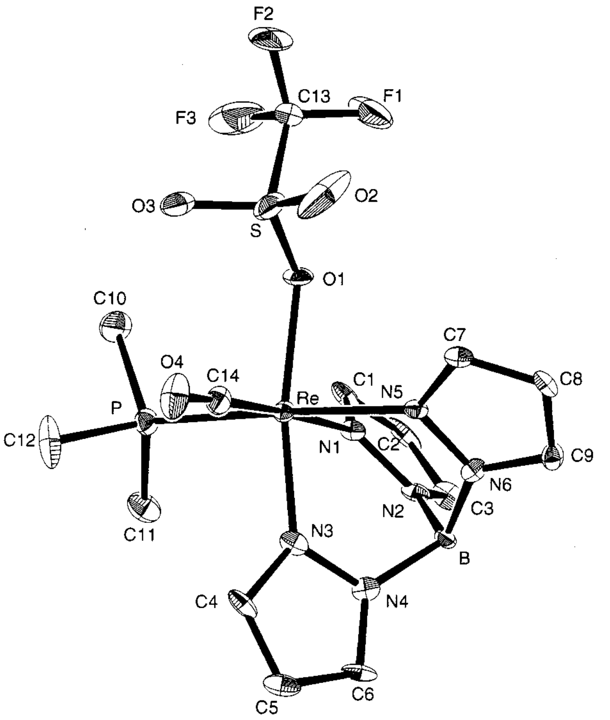

Figure 2. ORTEP diagram of TpRe(CO)(PMe$_3$)(OTf) (**10**) (30% probability ellipsoids).

Table 4. Selected Bond Distances (Å) and Angles (deg) for TpRe(CO)(PMe$_3$)(OTf) (10)

Re−P	2.398(2)	S−O1	1.489(6)
Re−N1	2.196(6)	S−O2	1.412(8)
Re−N3	2.052(7)	S−O3	1.421(7)
Re−N5	2.161(6)	O4−C14	1.15(1)
Re−C14	1.882(10)		
P−Re−O1	93.2(2)	O1−Re−C14	98.2(3)
P−Re−N1	90.2(2)	N1−Re−N3	87.9(2)
P−Re−N3	94.0(2)	N1−Re−C5	81.9(2)
P−Re−N5	171.8(2)	N1−Re−C14	176.0(3)
P−Re−C14	86.4(3)	N3−Re−N5	83.9(3)
O1−Re−N1	84.1(2)	N3−Re−C14	90.3(3)
O1−Re−N3	169.3(3)	N5−Re−C14	101.5(3)
O1−Re−N5	87.9(2)	Re−O1−S	123.0(4)

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[47] The majority of the protons of complex **7** were located in the Fourier map. However, due possibly to disorder, H(3) and H(17) were not located in the Fourier map, and these hydrogens were placed at calculated positions.

the prolonged heating period is problematic due to DME polymerization.

The covalent binding of the triflate moiety by the rhenium metal center was confirmed by a solid-state X-ray diffraction structural study. Suitable crystals for a structural study were grown by slow diffusion of hexanes into a methylene chloride solution of **10**. Crystal data are presented in Table 2, selected bond distances and angles are depicted in Table 4, and an ORTEP diagram is shown in Figure 2. The rhenium−oxygen bond length of 2.140(6) Å indicates a covalent linkage between the triflate ligand and the metal center. This distance is longer than the rhenium−triflate oxygen bond distances in the related complex TpRe(OTf)$_2$(O) (average distance 2.014 Å).[48] The decreased interaction between the triflate ligand and rhenium for **10** compared to TpRe(OTf)$_2$(O) is likely due to the increased electron density at the metal center for complex **10** {Re(II) vs Re(V)}. The sulfur−oxygen bond of the oxygen that is bound to the metal center is lengthened relative to the other two sulfur−oxygen bond distances (1.489(6) Å vs 1.412(8) and 1.421(7) Å). The rhenium−pyrazolyl nitrogen bond distance that is trans to the triflate ligand is elongated compared to the other two pyrazolyl bond distances (2.052(7) Å vs 2.196(6) and 2.161(6) Å).

Triflate is known to be a weakly coordinating ligand,[49] and the reduction of **10** to the putative anionic complex {[TpRe^I(CO)(PMe$_3$)(OTf)]$^-$} provides access to the {TpRe^I(CO)(PMe$_3$)} fragment after triflate dissociation. Thus, the reaction of **10** with Na/Hg in the presence of excess naphthalene yields TpRe(CO)(PMe$_3$)(η^2-naphthalene) (**12**) in 55% yield after workup (Scheme 2). Two coordination diastereomers are possible for complex **12** due to the potential binding of two distinct enantiofaces of the prochiral aromatic compound to the asymmetric metal center. In addition, two rotational isomers of each diastereomer are possible. Spectroscopic evidence indicates the selective formation of a single isomer for complex **12**. Complex **12** is characterized by $\nu_{CO} = 1825$ cm^{-1} (KBr) in its IR spectrum and $E_{1/2} = 0.19$ V (vs NHE) in its cyclic voltammogram. The oxidation wave is only partially reversible, and the reversibility was found to be dependent on the scan rate. Thus, at the Re^{II} oxidation state the Re−naphthalene complex decomposes on the timescale of the cyclic voltammetry experiment. Resonances for the bound protons are observed at 4.26 and 3.04 ppm in the ^{1}H NMR spectrum, and resonances for the bound carbons are assigned as peaks at 57.4 and 53.1 ppm in the ^{13}C NMR spectrum. Similar to the cyclohexene complex **7**, the naphthalene complex **12** has a high-field resonance (−23.4 ppm) in its ^{31}P{^{1}H} spectrum (see Table 1).

Reduction of TpRe(CO)(PMe$_3$)(OTf) (**10**) in the presence of excess phenanthrene in DME results in the precipitation of a bright yellow-green solid. Characterization of the product identified it as TpRe(CO)(PMe$_3$)(9,10-η^2-phenanthrene) (**13**) (27%, Scheme 2). Dihapto-binding of phenanthrene across C(9) and C(10) is indicated by spectroscopic features of complex **13**. The observation of two doublets of doublets (each proton is coupled to the other bound proton as well as phosphorus) for the two bound protons in the ^{1}H NMR spectrum of **13** provides strong evidence for binding to the internal ring of phenanthrene. Coordination to an external ring should yield a doublet of doublets as well as a doublet of doublet of doublets. The electronic preference for dihapto-binding of the internal ring (versus an external ring) of phenanthrene has been discussed.[50] Interestingly, one of the Tp doublets is shifted upfield (6.21 ppm) compared to other complexes of {TpRe(CO)(PMe$_3$)}, and we attribute this anomaly to shielding by the ring current of one of the phenanthrene aromatic rings.

Starting with the cyclohexene complex **7**, TpRe(CO)(PMe$_3$)(η^2-furan) (**14**) can be synthesized and isolated in 81% yield (Scheme 2). In contrast to the naphthalene complex **12**, two isomers are observed for **14** (2.1:1.0 ratio), and these isomers have been assigned as diastereomers (vide infra). Characterization details for **14** are similar to the naphthalene complex **12** (Table 1). Consistent with [Os(NH$_3$)$_5$(η^2-furan)][OTf]$_2$,[51] the d^5/d^6 oxidation wave for the furan complex **14** is irreversible at scan rates up to 500 mV/s; however this wave for **14** ($E_{p,a}$) is about 400 mV lower than for its osmium analogue.[51]

TpRe(CO)(PMe$_3$)(η^2-thiophene) (**15**) can be isolated as a pale yellow solid in 77% yield starting from **7** (Scheme 2). Multiple coordination modes have been observed for this and related sulfur-containing heterocycles.[52,53] Complex **15** exists as a mixture of three isomers, and these isomers have been assigned as two η^2-bound diastereomers (3.2:2.0 ratio) and an η^1-bound species (η^2/η^1 ratio $= 5.2{:}1.0$). Spectroscopic features for the dihapto-bound thiophene isomers are listed in Table 1. Resonances for the thiophenic protons of the η^1-bound isomer are observed as multiplets at 7.43 and 7.13 ppm. The observation of only two multiplets for η^1-coordinated thiophene indicates that the two α- and two β-protons are exchanged by a rapid Re−S bond rotation and S inversion. Of note, broadening of these resonances is not observed at room temperature. Interestingly, the IR spectrum of **15** exhibits a single absorption due to CO (1826 cm^{-1}), and a cyclic voltammogram of **15** displays a single quasi-reversible oxidation wave at $E_{1/2} = 0.01$ V (vs NHE). The 2-methylthiophene analogue **16** was prepared in a manner similar to **15** and was found to exist in an approximately 3:2:1 ratio of isomers, the latter of which corresponding to the *S*-bound isomer.

A similar synthetic sequence utilized for the formation of **12**−**16** allowed the coordination of acetone by the {TpRe(CO)(PMe$_3$)} moiety (Scheme 2). Two resonances for diastereotopic methyl groups are observed at 2.25 and 0.98 ppm in the ^{1}H NMR of TpRe(CO)(PMe$_3$)(η^2-acetone) (**17**). The upfield chemical shift of one methyl group ($\Delta\delta = 1.27$ ppm) likely indicates that this methyl group is in the shielding region of two pyrazolyl rings,[54,55] and this suggests that the oxygen of the bound acetone is syn to the PMe$_3$ ligand. Consistent with this assign-

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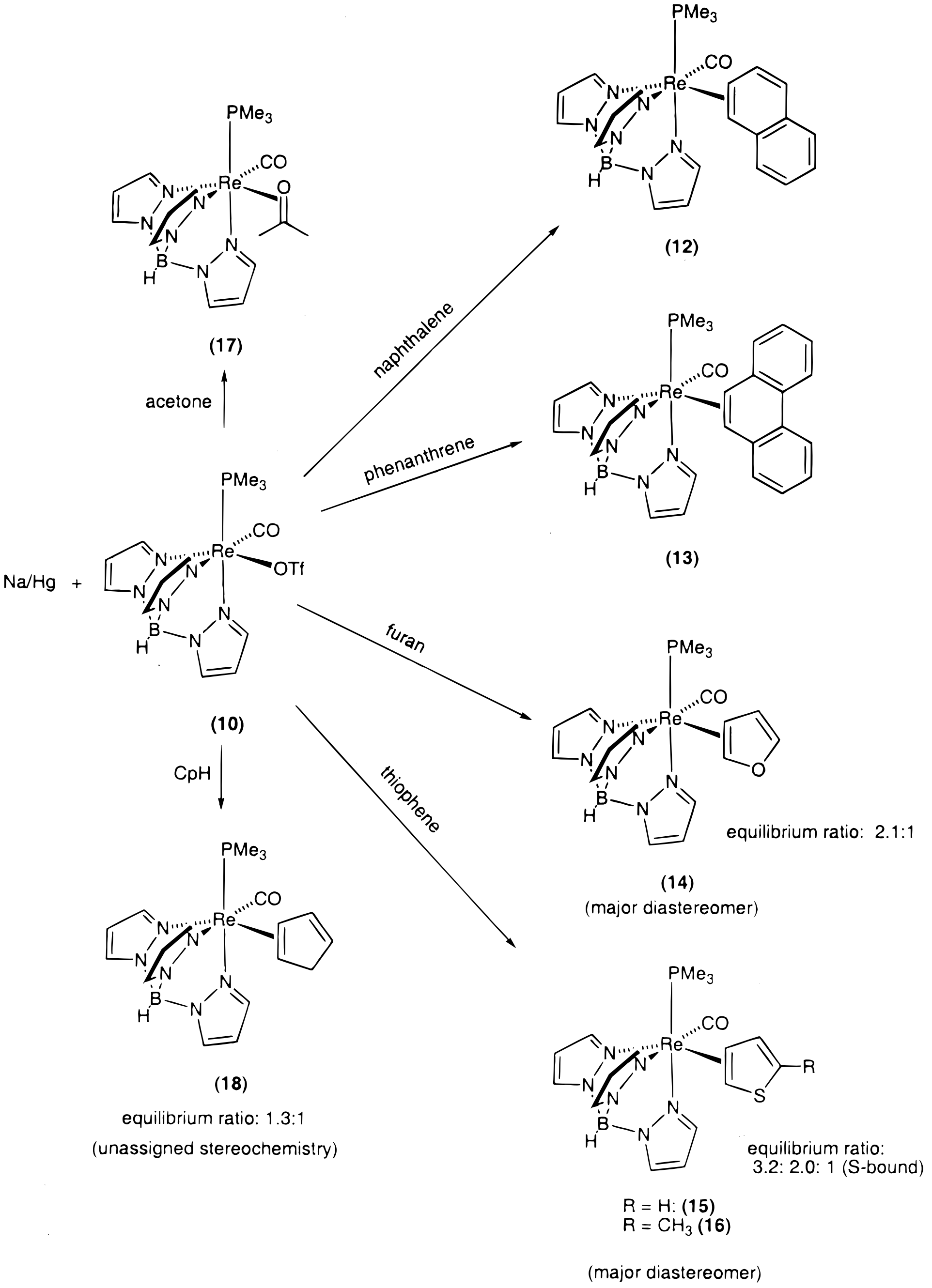
(48) Brown, S. N.; Mayer, J. M. *J. Am. Chem. Soc.* **1996**, *118*, 12119.
(49) Lawrance, G. A. *Chem. Rev.* **1986**, *86*, 17.
(50) Chin, R. M.; Dong, L.; Duckett, S. B.; Partridge, M. G.; Jones, W. D.; Perutz, R. N. *J. Am. Chem. Soc.* **1993**, *115*, 7685.
(51) Chen, H.; Liu, R.; Myers, W. H.; Harman, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 509.
(52) Angelici, R. J. *Coord. Chem. Rev.* **1990**, *105*, 61.
(53) Rauchfuss, T. B. *Prog. Inorg. Chem.* **1991**, *39*, 259.
(54) Feng, S. G.; White, P. S.; Templeton, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 2951.
(55) Gunnoe, T. B.; White, P. S.; Templeton, J. L. *Organometallics* **1997**, *16*, 370.

Scheme 2. Preparation of TpRe(CO)(PMe)$_3$(η^2-L) (where L = naphthalene, phenanthrene, furan, thiophene, acetone, or cyclopentadiene)



ment is the lack of coupling between phosphorus and the bound acetone carbon in the ^{13}C NMR spectrum of **17**. As a consequence of η^2-coordination, the ketone carbonyl resonates at 84.2 ppm in the ^{13}C NMR spectrum.[56] Numerous dihapto-bound ketone complexes have been reported,[57–80] but most of these examples are

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(56) Helberg, L. E.; Gunnoe, T. B.; Brooks, B. C.; Sabat, M.; Harman, W. D. *Organometallics* **1999**, *18*, 573.

(57) Clemens, J.; Green, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1973**, 375.

(58) Countryman, R.; Penfold, B. R. *J. Chem. Soc., Chem. Commun.* **1971**, 1598.

(59) Ittel, S. D. *J. Organomet. Chem.* **1977**, *137*, 223.

(60) Ittel, S. D. *Inorg. Chem.* **1977**, *16*, 2589.

(61) Green, M.; Howard, J. A. K.; Laguna, A.; Smart, L. E.; Spencer, J. L.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1977**, 278.

(62) Burgess, J.; Chambers, J. G.; Clarke, D. A.; Kemmitt, R. D. W. *J. Chem. Soc., Dalton Trans.* **1977**, 1906.

(63) Clarke, D. A.; Hunt, M. M.; Kemmitt, R. D. W. *J. Organomet. Chem.* **1979**, *175*, 303.

(64) Grassi, A.; Longo, P.; Musco, A.; Porzio, W.; Scrivanti, A. *J. Organomet. Chem.* **1985**, *289*, 439.

(65) Klein, D. P.; Dalton, D. M.; Méndez, N. Q.; Arif, A. M.; Gladysz, J. A. *J. Organomet. Chem.* **1991**, *412*, C7.

(66) Williams, D. S.; Schofield, M. H.; Anhaus, J. T.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 6728.

(67) Barry, J. T.; Chacon, S. T.; Chisholm, M. H.; Huffmann, J. C.; Streib, W. E. *J. Am. Chem. Soc.* **1995**, *117*, 1974.

(68) Harman, W. D.; Fairlie, D. P.; Taube, H. *J. Am. Chem. Soc.* **1986**, *108*, 8223.

(69) Burkey, D. J.; Debad, J. D.; Legzdins, P. *J. Am. Chem. Soc.* **1997**, *119*, 1139.

(70) Bryan, J. C.; Mayer, J. M. *J. Am. Chem. Soc.* **1990**, *112*, 2298.

(71) Powell, D. W.; Lay, P. A. *Inorg. Chem.* **1992**, *31*, 3542.

(72) Tsou, T. T.; Huffman, J. C.; Kochi, J. K. *Inorg. Chem.* **1979**, *18*, 2311.

(73) Harman, W. D.; Sekine, M.; Taube, H. *J. Am. Chem. Soc.* **1988**, *110*, 2439.

with electron-deficient ketones. The irreversible oxidation wave (irreversible up to 500 mV/s; $E_{p,a} = 0.26$ V vs NHE 100 mV/s) is likely a consequence of the ability of the acetone ligand to access an η^1-oxygen bound coordination isomer. In support of this, a reduction wave at -0.39 V is observed only after an oxidative scan through 0.26 V.

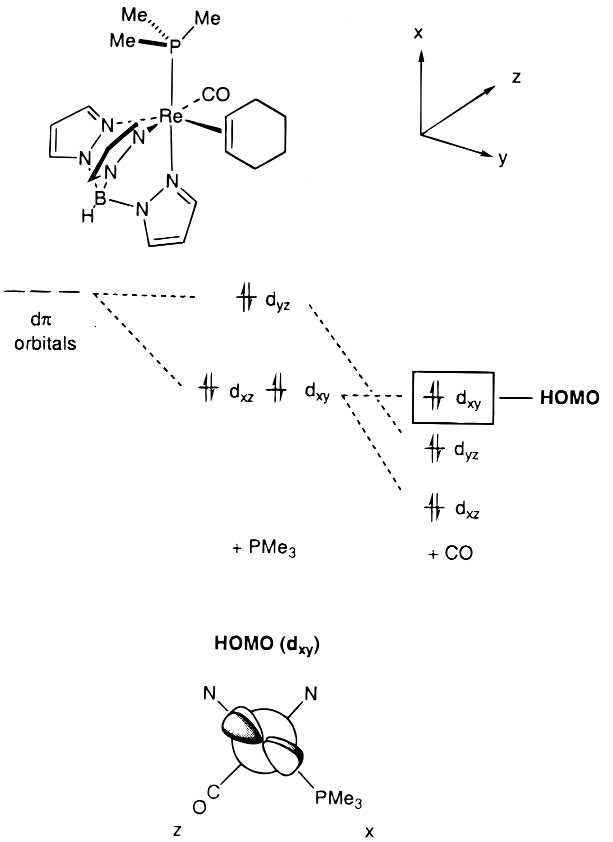
The compound TpRe(CO)(PMe$_3$)(η^2-cyclopentadiene) (**18**) was prepared in a manner similar to the procedure used for the naphthalene complex **12.** Analytically pure **18** was isolated after chromatography in 55% yield as a 1.6:1.0 ratio of diastereomers. Over a period of hours (>100 h) the ratio changed to 1.3:1.0. The slow rate of exchange places the $\Delta G^{\ddagger}$ for this process ($k \approx 3.5 \times 10^{-6}$; $\Delta G^{\ddagger} \approx 25$ kcal/mol) close to that observed for complexes of the form [Cp^{x}Re(NO)(PPh$_3$)(η^2-alkene)]$^+$.[26,37] Due to the reversibility of the diastereomer interconversion, the rate constant for the forward process was calculated from the k_{obs} and K_{eq}.[81]

Discussion

Of paramount importance to our synthetic goals is a rational understanding of the stereochemical features of the {TpRe(CO)(PMe$_3$)} fragment. Due to dπ to π* back-bonding, the C−C double bond of the cyclohexene complex **7** will electronically prefer to align parallel to the Re−PMe$_3$ bond axis and orthogonal to the Re−CO bond axis. A qualitative molecular orbital diagram and the proposed HOMO for the {TpRe(CO)(PMe$_3$)} moiety are depicted in Scheme 3. If the x-axis is defined along the Re−P bond and the z-axis is defined along the Re−CO bond, then dπ back-bonding with PMe$_3$ would lower the energy of the d$_{xy}$ and d$_{xz}$ orbitals while the interaction with carbon monoxide would lower the energy of the d$_{xz}$ and d$_{yz}$ orbitals. Since carbon monoxide is a more prolific π-acid than trimethylphosphine, the d$_{xy}$ orbital would remain highest in energy, and it is this orbital with which the π* orbital of the C−C bond of the olefin can best interact. A similar analysis has been made for olefin complexes of [Cp^{x}Re(NO)(PPh$_3$)]$^+$.[26] The solid-state structure determination of the cyclohexene complex **7** confirms that the C=C bond is aligned approximately parallel to the Re−P bond (vide supra).

A potential advantage of developing dearomatization methodologies with rhenium(I) complexes is the possibility of utilizing chiral metal centers for enantioselective dearomatization reactions. The development of synthetic routes to access a variety of systems of the type {TpRe(CO)(L)} would provide the opportunity to systematically adjust the steric and electronic environment of the chiral rhenium metal center.[82] Given our goals of asymmetric manipulation of η^2-aromatic ligands, careful scrutiny of the stereochemical features of the {TpRe(CO)(PMe$_3$)} fragment seemed appropriate. Thus, we sought the assignment of the major coordination diastereomers of the TpRe(CO)(PMe$_3$)(η^2-L) complexes {L = naphthalene (**12**), furan (**14**), thiophene (**15**), or acetone (**17**)}. A combination of proton decoupling experiments and one-dimensional NOE (nuclear Overhauser enhancement) measurements were used to determine the stereochemistry of the major diastereomers shown in Scheme 2.

Scheme 3. Qualitative Molecular Orbital Diagram for TpRe(CO)(PMe$_3$)(η^2-cyclohexene) (7) and Depiction of the dπ HOMO



Due to dπ to ligand back-bonding, the unsaturated ligands will prefer to align their bond axis parallel to the Re−P bond axis (vide supra). As mentioned above, for complexes **12**, **14**, and **15** four stereoisomers (two rotational isomers and two coordination diastereomers) are possible (Scheme 4). For the naphthalene complex **12** only a single isomer is spectroscopically observed. However, two isomers are observed for the furan complex **14** and the thiophene complex **15**, and these isomers have been assigned as coordination diastereomers. Diastereomers rather than rotational isomers are implicated by the observation that for the cyclohexene complex **7** and the phenanthrene complex **13** (diastereomers are not possible) only a single isomer is observed (in Scheme 4, structures **I** and **IV** are identical for these systems, as are structures **II** and **III**). Furthermore, modeling studies of these complexes indicate that rotational isomers which place the bulk of the unsaturated ligand syn to the Tp ligand are highly destabilized

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(74) Harman, W. D.; Dobson, J. C.; Taube, H. *J. Am. Chem. Soc.* **1989**, *111*, 3061.

(75) Hill, J. E.; Fanwick, P. E.; Rothwell, I. P. *Organometallics* **1992**, *11*, 1771.

(76) Okuda, J.; Herberich, G. E. *Organometallics* **1987**, *6*, 2331.

(77) Erker, G.; Dorf, U.; Czisch, P.; Petersen, J. L. *Organometallics* **1986**, *5*, 668.

(78) Wood, C. D.; Schrock, R. R. *J. Am. Chem. Soc.* **1979**, *101*, 5421.

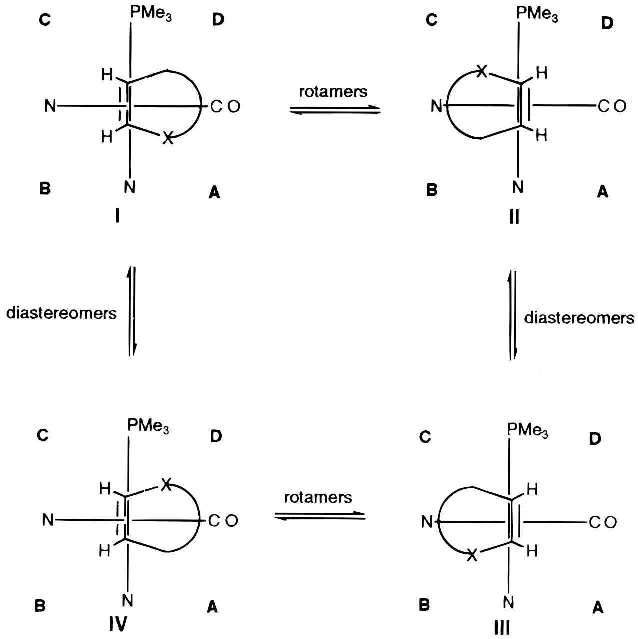
(79) Mayer, J. M.; Bercaw, J. E. *J. Am. Chem. Soc.* **1982**, *104*, 2157.

(80) Chisholm, M. H.; Folting, K.; Klang, J. A. *Organometallics* **1990**, *9*, 607.

(81) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981.

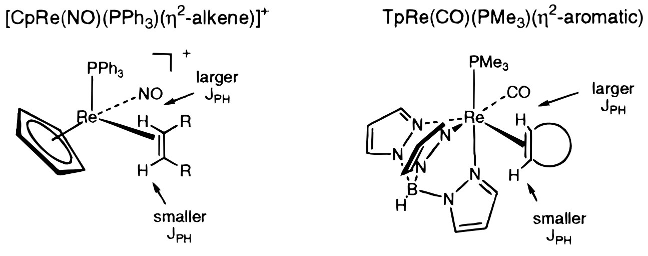
(82) We have obtained synthetic access to fragments of the type {TpRe(CO)(L)} where L = pyridine, 3-methylimidazole, thiazole, NH$_3$, and ^{t}BuNC. Unpublished results.

Scheme 4. Stereochemical Analysis for the System TpRe(CO)(PMe$_3$)(η^2-L) (where L is an olefinic or aromatic molecule)



(**II** or **III** in Scheme 4).[83] Finally, the synthesis of the complex TpRe(CO)(PMe$_3$)(4,5-η^2-2-methylthiophene) (**17**) provided additional evidence for diastereomers rather than rotational isomers. If the two observed isomers of the thiophene complex **15** (discounting the monohapto-bound isomer) were due to rotational conformers, the ratio of these isomers would be expected to be substantially altered with the 2-methyl-substituted thiophene (Scheme 4). However, if the two species observed for **15** were the diastereomers **I** and **IV** shown in Scheme 4, the 2-methyl substituent for each isomer would be oriented toward the carbonyl ligand, minimizing any significant steric interactions. Judging from NMR data, the isomer ratio of the 2-methylthiophene complex **16** is 1.5:1.0 (ignoring the η^1-bound isomer), which is an insignificant change from the thiophene complex **15** (1.6:1.0). Thus, the choice of potential isomers can be narrowed to the two potential diastereomers with the bulk of the ligand syn with the carbonyl ligand (**I** and **IV** in Scheme 4).

Scheme 5. Magnitude of Phosphorus–Hydrogen Coupling Constant for TpRe(CO)(PMe$_3$)(η^2-L) Complexes 7, 8, 12–15, 17, and 18



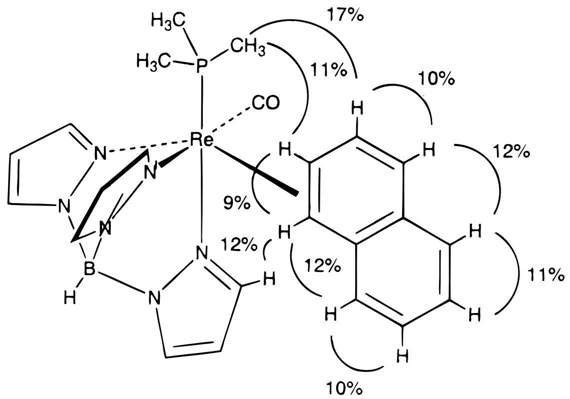


Figure 3. NOE data for naphthalene complex **12**.

As mentioned above, the {TpRe(CO)(PMe$_3$)} fragment is structurally and electronically similar to the {[Cp^x-Re(NO)(PPh$_3$)]$^+$} moieties, which have received significant attention from Gladysz et al.[26] Importantly, large differences in phosphine–hydrogen coupling constants for the [Cp^{x}Re(NO)(PPh$_3$)(η^2-alkene)]$^+$ complexes have been observed for the protons of the bound carbons.[26,35–39,84] In particular, the olefinic proton(s) oriented toward the phosphine display J_{PH} values that are dramatically larger than those oriented away from the phosphine (Scheme 5). Analogous differences in coupling constants are observed for the aromatic complexes **12**–**15**. For example, the bound protons for the naphthalene complex **12** resonate at 4.26 and 3.04 ppm with J_{PH} = 13 and 2 Hz, respectively. Thus, the resonance at 4.26 ppm is assigned as the proton syn to the phosphine ligand. In accordance with this conclusion is the 11% NOE observed between the phosphine ligand and the resonance at 4.26 ppm as well as the 12% NOE observed between the 3.04 ppm resonance and a Tp doublet (Figure 3). A final confirmation of the bound proton assignment is derived from the relative chemical shifts for all of the aromatic complexes. The bound protons that are syn to the pyrazolyl ring are consistently shifted upfield, and we attribute this shift to the shielding from the ring current of two pyrazolyl rings (vide supra). Utilizing proton coupling and NOE data, the uncoordinated ring of the naphthalene complex **12** was determined to be anti to the phosphine ligand (see Scheme 2). All NOE data were in agreement with this conclusion (Figure 3).

Rapid interconversion of two diastereomers for complex **12** could yield a time-averaged NMR spectrum and appear as though only a single diastereomer were present. However, on the basis of similar reduction potentials and substitution rates, we presume that interconversion rates for **12** are similar in magnitude to those of {Os(NH$_3$)$_5$}$^{2+}$.[9] In addition, the observation of two diastereomers for other TpRe(CO)(L)(η^2-naphthalene) (L = ^{t}BuNC or pyridine) complexes supports our notion that **12** is present as a single diastereomer.[85] Perhaps the most reliable evidence for a single diastereomer for complex **12** is derived from variable-temperature ^{1}H NMR experiments. Cooling a methylene chloride-d_2 solution of **12** to −60 °C yields a ^{1}H NMR spectrum virtually identical to that taken at 20 °C, and no resonance due to a second diastereomer or line-broadening is detectable.

Stereochemical features of complexes formed from chiral metal centers and prochiral ligands (e.g., olefins) have been analyzed by utilizing four quadrants corre-

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(83) Calculations were performed at the MM2 level of theory.

(84) Fernández, J. M.; Gladysz, J. A. *Organometallics* **1989**, *8*, 207.

(85) Unpublished results.

sponding to the steric properties of each vinylic position (Scheme 4).[26,86,87] The prochiral aromatic ligands furan, thiophene, and naphthalene are similar to unsymmetrically disubstituted cis olefins.

As mentioned previously, four isomers are possible for the series of prochiral aromatic complexes. The sterically imposing pyrazolyl ring would be expected to selectively stabilize structures **I** and **IV** in Scheme 4 relative to isomers **II** and **III**. In other words, the defining difference between quadrants **B**/**C** and **A**/**D** and, hence, the predisposition for **I**/**IV** over **II**/**III**, is the steric discrepancy between the CO ligand and the trans pyrazolyl ring. Given that the trimethylphosphine ligand is more sterically encumbering than the pyrazolyl ring trans to it, any substituents of the aromatic ring would likely be preferentially directed to quadrant **A**, and this is indeed the isomer observed for the naphthalene complex **12**. The crystal structure of TpRe(CO)(PMe$_3$)-(η^2-cyclohexene) (**7**) (vide supra) supports the conclusion that the PMe$_3$/CO sector (labeled **D** in Scheme 4) is more sterically demanding than the trans pyrazolyl/CO sector (labeled **A** in Scheme 4). The Re−C bond length for the carbon syn to the relatively bulky phosphine ligand is approximately 0.04 Å longer than the Re−C bond distance for the carbon anti to the phosphine ligand. This significant difference in bond distance is attributed to the steric bulk of the phosphine ligand compared to the trans pyrazolyl ring. In addition, a proton of the pyrazolyl ring trans to the phosphine has a steric interaction with one of the methylene protons of the cyclohexene ring (1.964 Å between the two protons, vide supra). However, this interaction should be less consequential for ligands with sp^2-hybridized carbons adjacent to the coordinated double bond, and thus the impact of the steric directing ability of the phosphine ligand will be enhanced for the naphthalene complex **12**. Therefore, it is a combination of electronic and steric factors that results in a single stereoisomer for complex **12**. The electronic nature of the metal "locks" the naphthalene ligand into a preferred orientation with the bound carbon−carbon double bond orthogonal to the Re−CO bond axis, and the steric bulk of the phosphine ligand renders the diastereomer with the unbound ring anti to it more thermodynamically stable.

Unlike the naphthalene complex **12**, the furan complex **14** is observed as a mixture of diastereomers. This could be expected given the sterically similar nature of the unbound β-methine group and the oxygen. The major diastereomer has been assigned as that with the oxygen oriented away from the phosphine ligand (Scheme 2). NOE, coupling data, and the relative chemical shifts of the bound protons of the two isomers support this conclusion. Thus, NOEs of 7% are observed between the bound and unbound β-protons of the major isomer and the phosphine ligand, and an 8% NOE is observed between the bound α-proton of the minor diastereomer and the phosphine ligand. The major diastereomer also displays a 5% NOE between the bound α-proton and a Tp doublet. Given that the bound α-proton of the major diastereomer is expected to be shielded by the ring-current of two pyrazolyl rings (vide supra), the chemical shift difference between the two bound protons of the major diastereomer should be reduced in comparison to that of the minor diastereomer. The $\Delta\delta$ for the bound protons of the major diastereomer is 1.47 ppm, while that of the minor diastereomer is 4.21 ppm.

Harris has studied thiophene coordination modes utilizing Fenske−Hall molecular orbital calculations.[88,89] For thiophene ligands donating two electrons to the metal center, two coordination modes have been observed. Monohapto-coordination through the sulfur atom is by far the most commonly observed two-electron-donating coordination mode for thiophene; however, thiophene can also bind η^2 through two carbon atoms. It has been suggested that η^1-sulfur-bound thiophene is a poor π-acid.[88,90] To our knowledge, the only other metal fragment to this date that demonstrates a thermodynamic preference for η^2-coordination of thiophene is $\{Os(NH_3)_5\}^{2+}$.[91,92] Thus, the thermodynamic preference of the {TpRe(CO)(PMe$_3$)} fragment for dihapto-binding of thiophene indicates that this metal system is a strong π-base.

Assignment of the major and minor diastereomer for the thiophene complex **15** was complicated by the presence of through-sulfur "W-coupling" between the α-protons. However, through the experiments mentioned above for the furan complex **14** the major diastereomer was ultimately assigned as the isomer with the sulfur atom oriented anti to the phosphine ligand. In support of this assignment, a 9% NOE is observed between the bound β-proton of the major diastereomer and trimethylphosphine, and a 5% NOE is noted between the bound β-proton and the unbound β-proton. Of note, the lack of a NOE between the two α-protons (for both diastereomers) confirms the assigned position of the sulfur atom. Notably, the bound α-proton for the major diastereomer is actually shifted upfield relative to the bound β-proton due to the ring-current of the pyrazolyl rings. The result is a $\Delta\delta$ of −0.82 ppm for the major diastereomer and 1.07 ppm for the minor diastereomer ($\Delta\delta = \delta_\alpha - \delta_\beta$).

The orientation of the acetone complex **17** has been assigned as having the oxygen syn to the phosphine ligand. The lack of an NOE between the phosphine ligand and the methyl groups of the acetone ligand supports this conclusion. In contrast, irradiation of the upfield methyl group (0.98 ppm) results in an NOE with the pyrazolyl ring, and an NOE is observed between the downfield methyl resonance (2.25 ppm) and the same pyrazolyl proton. Coordination of the phenanthrene compound at the internal ring does not offer the possibility of two enantiofaces, and thus diastereomers are not possible. However, one of the bound protons is shielded relative to the other ($\Delta\delta$ = 1.97 ppm) and is consistent with this trend for the other aromatic complexes (vide supra).

Stability and Ligand Exchange Reactions. The naphthalene, furan, and thiophene complexes all undergo ligand exchange reactions with acetone with

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[86] Kolb, H. C.; VanNieuwenhze, M. S.; Sharpless, K. B. *Chem. Rev.* **1994**, 2483.

[87] Sharpless, K. B.; Amberg, W.; Beller, M.; Chen, H.; Hartung, J.; Kawanami, Y.; Lubben, D.; Manoury, E.; Ogino, Y.; Shibata, T.; Ukita, T. *J. Org. Chem.* **1991**, *56*, 4585.

[88] Harris, S. *Organometallics* **1994**, *13*, 2628.

[89] Harris, S. *Polyhedron* **1997**, *16*, 3219.

[90] Palmer, M. S.; Rowe, S.; Harris, S. *Organometallics* **1998**, *17*, 3798.

[91] Spera, M. L.; Harman, W. D. *Organometallics* **1995**, *14*, 1559.

[92] Spera, M. L.; Harman, W. D. *J. Am. Chem. Soc.* **1997**, *119*, 8843.

Table 5. Half-Lives and Activation Energy for Ligand Exchange Reactions with Acetone

complex	$\Delta G^{\ddagger}$ (kcal/mol; 23 °C)	$t_{1/2}$ (h)
TpRe(CO)(PMe$_3$)(η^2-naphthalene) (**10**)	23.3	5.9
TpRe(CO)(PMe$_3$)(η^2-furan) (**14**)	25.3	168
TpRe(CO)(PMe$_3$)(η^2-thiophene) (**15**)	25.1	134

varying rates. The exchange reactions are all quantitative in acetone-d_6, and the formation of TpRe(CO)(PMe$_3$)(η^2-acetone-d_6) (**17**) is accompanied by the appearance of resonances in the proton NMR for the free aromatic compounds. The $t_{1/2}$ and $\Delta G^{\ddagger}$(23 °C) for each ligand exchange are presented in Table 5. Oxidative addition or insertion into metal heteroatom bonds is not observed at room temperature for complex **12**, **14**, or **15**.[53,93] As mentioned above, no evidence for the decomposition of TpRe(CO)(PMe$_3$)(η^2-cyclohexene) (**7**) was obtained upon prolonged refluxing in hexanes.

Of note, related Cp^{x}Re(I) complexes of aromatic molecules have been reported to participate in C−H oxidative addition reactions.[94−97] Although reaction conditions differ somewhat, we have seen no indication of oxidative addition for the aromatic complexes reported herein. Indeed several recent studies suggest that octahedral Tp complexes are less prone to undergo oxidative addition than their Cp analogues.[98−101] Whether this is a result of inductive (i.e., electronic) or geometrical differences or both is not well understood.

Finally, we draw a comparison of the present work with the previously reported complex [(dien)Re(CO)(PPh$_3$)(η^2-furan)][OTf] (dien = diethylenetriamine).[102] The dien−rhenium system is electronically similar to the {TpRe(CO)(PMe$_3$)} fragment. For example, [(dien)Re(CO)(PPh$_3$)(η^2-furan)][OTf] shows a $\nu_{CO} = 1814$ cm^{-1} in its IR spectrum and $E_{p,a} = 0.61$ V in its cyclic voltammogram, while the Tp rhenium furan complex **14** has a $\nu_{CO} = 1826$ cm^{-1} and $E_{p,a} = 0.30$ V. In contrast to TpRe(CO)(PMe$_3$)(η^2-furan) (**14**), [(dien)Re(CO)(PPh$_3$)(η^2-furan)][OTf] decomposes in acetonitrile with $t_{1/2} \approx 1$ day (cf. $t_{1/2} = 7$ days for **14**). A comparison of the electrochemical and infrared data for these two compounds indicates that the Tp-based system is more electron-rich and thus a better π-base than the dien analogue. This factor along with the difference in size of the phosphine accounts for the increased stability of **14**.

Summary and Conclusions

To find a synthetic surrogate for the {Os(NH$_3$)$_5$}$^{2+}$ fragment, it is necessary to access a 16-electron metal species that both acts as a strong π-base (i.e., is strongly back-donating) and is unlikely to undergo oxidative addition reactions, which are common with electron-rich transition metal complexes and aromatic compounds. The{TpRe(CO)(PMe$_3$)} metal system is a strongly π-basic entity as evidenced by the characterization features of the TpRe(CO)(PMe$_3$)(η^2-cyclohexene) (**7**) complex (vide supra), the ability to bind naphthalene in an η^2-coordination mode, the thermodynamic preference for η^2-thiophene over η^1-thiophene, and the proclivity for forming stable π complexes with acetone rather than the more common σ-bound species.[103] In addition, the aromatic complexes **12, 14**, and **15** undergo clean ligand exchange reactions with no signs of oxidation addition or insertion into carbon−heteroatom bonds. Ultimately, the ability to systematically vary the steric and electronic properties of “L” in {TpRe(CO)(L)}[82] should provide a series of potential dearomatization reagents that allow fine-tuning of properties for specific synthetic purposes.

Abbreviations. DME = 1,2-dimethoxyethane; THF = tetrahydrofuran; TBAH = tetrabutylammonium-hexafluorophosphate; Tp = hydridotris(pyrazolyl)borate; OTf = trifluoromethanesulfonate (triflate); DMA = *N*,*N*-dimethylacetamide.

Experimental Section

General Methods. Electrochemical experiments were performed under a dinitrogen atmosphere using a PAR model 362 potentiostat driven by a PAR model 175 universal programmer. Cyclic voltammograms were recorded at 100 mV/s (20 °C) in a standard three-electrode cell from +1.80 to −1.80 V (unless otherwise noted) with a glassy carbon working electrode, DMA solvent, and TBAH electrolyte. All potentials are reported vs NHE (normal hydrogen electrode) using cobaltocenium hexafluorophosphate ($E_{1/2} = -0.78$ V) or ferrocene ($E_{1/2} = 0.55$ V) as internal standard. Unless otherwise noted, all synthetic reactions and electrochemical experiments were performed under a dry nitrogen atmosphere. Methylene chloride, THF, DME (1,2-dimethoxyethane), and hexanes were purified by passage through a column packed with activated alumina.[104]

Sodium mercury amalgam (5%), cyclohexene, cyclopentene, trimethylphosphine, phenanthrene, and naphthalene were used as purchased from Aldrich Chemical Co. Dicyclopentadiene was heated to reflux for approximately 4 h and then distilled prior to use (cyclopentadiene). Deactivated alumina was approximately activity level V. TpRe(Cl)$_2$(O) (**4**) was prepared using the method reported by Mayer and Brown,[30] KTp was prepared according to a published procedure,[105] and TpRe(CO)$_2$(THF) was prepared as previously described.[27,106]

TpRe(CO)(PMe$_3$)(η^2-cyclohexene) (7). Benzene (75 mL) and TpRe(Cl)$_2$(PMe$_3$) (**6**) (0.5090 g, 0.932 mmol) were combined in a two-neck round-bottom flask. To the resulting orange slurry was added cyclohexene (1.9 mL, 18.7 mmol, 20 equiv) followed by sodium mercury amalgam (5% sodium, 1.0337 g, 2.25 mmol, 2.4 equiv based on **6**). The reaction solution was purged with CO (g) for approximately 10 min and then stirred in an oil bath at 60 °C for approximately 14 h (with a slow CO(g) purge over the solution). Next, the solution was cooled to room temperature, purged with dinitrogen for approxi-

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(93) Angelici, R. J. *Polyhedron* **1997**, *16*, 3073.

(94) Bergman, R. G.; Seidler, P. F.; Wenzel, T. T. *J. Am. Chem. Soc.* **1985**, *107*, 4358.

(95) Wenzel, T. T.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 4856.

(96) Leiva, C.; Sutton, D. *Organometallics* **1998**, *17*, 1700.

(97) For C−Cl activation, see: Leiva, C.; Sutton, D. *Organometallics* **1998**, *17*, 4568.

(98) Curtis, M. D.; Shiu, K. *Inorg. Chem.* **1985**, *24*, 1213.

(99) Curtis, M. D.; Shiu, K.-B.; Butler, W. M. *J. Am. Chem. Soc.* **1986**, *108*, 1550.

(100) Gelabert, R.; Moreno, M.; Lluch, J. M.; Lledós, A. *Organometallics* **1997**, *16*, 3805.

(101) Oldham, J. W. J.; Hinkle, A. S.; Heinekey, D. M. *J. Am. Chem. Soc.* **1997**, *119*, 11028.

(102) Brooks, B. C.; Chin, R. M.; Harman, W. D. *Organometallics* **1998**, *17*, 4716.

(103) Dalton, D. M.; Fernández, J. M.; Emerson, K.; Larsen, R. D.; Arif, A. M.; Gladysz, J. A. *J. Am. Chem. Soc.* **1990**, *112*, 9198.

(104) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(105) Trofimenko, S. *J. Am. Chem. Soc.* **1967**, *89*, 3170.

(106) Angaroni, M.; Ardizzoia, G. A.; D’Alfonso, G.; La Monica, G.; Masciocchi, N.; Moret, M. *J. Chem. Soc., Dalton Trans.* **1990**, 1895.

mately 15 min, and taken back into the glovebox. Vacuum filtration of the dark solution through a fine porosity frit was followed by solvent removal under a dinitrogen purge. Purification of the resulting oil on deactivated alumina with hexanes/diethyl ether (1:1) yielded a pale yellow eluent (approximately 250 mL of eluent was collected). Solvent removal of the yellow eluent provided a pale yellow solid, which was washed with hexanes (10 mL) and dried in vacuo (0.3309 g, 61% yield). IR (KBr): $\nu_{CO} = 1796$ cm-1; $\nu_{BH} = 2478$ cm^{-1}. ^{1}H NMR (acetone-d_6, δ): 8.14, 8.00, 7.80, 7.70, 7.43 (6H, 1:1:2(isochronous resonances):1:1, each a d, Tp C*H*), 6.24, 6.18 (3H, 2(isochronous resonances):1, each a t, Tp C*H*), 2.97, 2.68, 2.48, 1.72, 1.37 (10H, 2:2:1:3:2, each a m, cyclohexene protons), 1.25 (9H, d, $^2J_{PH} = 9$ Hz, P(CH_3)$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 200.4 (d, $^2J_{PC} = 8$ Hz, *C*O), 146.5, 143.6, 138.9, 135.9, 135.6, 135.4 (each a d of t, $^1J_{CH} = 185$ Hz, $J_{CH} = 8$ Hz, Tp *C*H, 3 and 5 position), 106.3, 105.7, 105.4 (each a d of t, $^1J_{CH} = 177$ Hz, $^2J_{CH} = 8$ Hz, Tp *C*H, 4 position), 51.2 (d, $^1J_{CH} = 151$ Hz, bound olefinic carbon), 49.1 (dd, $^1J_{CH} = 156$ Hz, $^2J_{PC} = 10$ Hz, bound olefinic carbon), 32.4 (td, $^1J_{CH} = 124$ Hz, $^3J_{PC} = 2$ Hz, α-methylene of cyclohexene), 31.6, 24.6, 24.4 (each a t, $^1J_{CH} = 124-126$ Hz, methylene carbons of cyclohexene), 16.4 (qd, $^1J_{CH} = 127$ Hz, $^1J_{PC} = 31$ Hz, P(*C*H$_3$)$_3$). ^{31}P{^{1}H} (acetone-d_6, δ): −18.1 (*P*Me$_3$). CV (DMA, TBAH, 50 mV/s): $E_{1/2} = 0.23$ V (II/I). Anal. Calcd for $C_{19}H_{29}BN_6OPRe$: C, 38.98; H, 4.99; N, 14.35. Found: C, 38.65; H, 5.30; N, 14.40.

TpRe(CO)(PMe$_3$)(η^2-cyclopentene) (8). Benzene (50 mL) and TpRe(Cl)$_2$(PMe$_3$) (**6**) (0.2031 g, 0.372 mmol) were combined in a pressure tube. The pressure tube was attached through a stainless steel coupling to a needle valve inlet. In addition, the pressure reactor was equipped with a pressure gauge and pressure release valve. To the resulting orange slurry was added cyclopentene (1.6 mL, 18.6 mmol, 50 equiv) followed by sodium mercury amalgam (5% sodium, 0.8334 g, 1.81 mmol, 4.9 equiv based on **6**). The pressure tube was sealed, evacuated, and back-filled with CO gas (35 psi). The reaction solution was stirred in an oil bath at 55 °C for approximately 14 h, cooled to room temperature, evacuated, and taken back into the glovebox. Vacuum filtration of the dark solution through a fine porosity frit was followed by solvent removal under reduced pressure. Dissolution of the resulting oil in methylene chloride/hexanes (15 mL/25 mL) and subsequent solvent removal in vacuo yielded a reddish-brown powder. The solid was washed with approximately 10 mL of hexanes and dried in vacuo. A pale orange solid was isolated in 68% yield (0.1454 g). IR (KBr): $\nu_{CO} = 1807$ cm^{-1}; $\nu_{BH} = 2456$ cm^{-1}. ^{1}H NMR (acetone-d_6, δ): 8.21, 8.03, 7.81, 7.80, 7.69, 7.57 (each 1H, each a d, Tp C*H*), 6.26, 6.24, 6.19 (each 1H, each a t, Tp C*H*), 3.27, 3.01, 2.06, 1.97, 1.44 (6H, 2:1:1:1:1, each a m, cyclopentene protons), 2.67 (1H, dd, $J = 13, 8$ Hz), 2.36 (1H, dd, $J = 13, 8$ Hz), 1.26 (9H, d, $^2J_{PH} = 9$ Hz, P(CH_3)$_3$). ^{13}C NMR (acetone-d_6, δ): 200.8 (d, $^2J_{PC} = 8$ Hz, *C*O), 147.0, 143.5, 140.3, 136.5, 136.3, 135.7 (each a d of t, $^1J_{CH} = 184-186$ Hz, $J_{CH} = 7$ Hz, Tp *C*H, 3 and 5 position), 106.8, 106.2, 106.1 (each a d of t, $^1J_{CH} = 176-178$ Hz, $^2J_{CH} = 8$ Hz, Tp *C*H, 4 position), 58.4 (d, $^1J_{CH} = 152$ Hz, bound olefinic carbon), 57.9 (d, $^1J_{CH} = 152$ Hz, bound olefinic carbon), 36.6 (m, α-methylene of cyclohexene), 23.2, 16.7 (each a t, $^1J_{CH} = 124$ Hz, methylene carbons of cyclopentene), 16.3 (qd, $^1J_{CH} = 127$ Hz, $^1J_{PC} = 32$ Hz, P(*C*H$_3$)$_3$). CV (DMA, TBAH, 100 mV/s): $E_{1/2} = 0.37$ V (II/I). Anal. Calcd for $C_{18}H_{27}BN_6OPRe$: C, 37.83; H, 4.76; N, 14.71. Found: C, 38.01; H, 4.84; N, 14.50.

TpRe(CO)(PMe$_3$)(OTf) (10). The cyclohexene complex **7** (0.1337 g, 0.228 mmol) was dissolved in approximately 20 mL of DME. To this pale yellow solution was added AgOTF (0.0594 g, 0.231 mmol, 1.01 equiv, dissolved in 5 mL of DME). Upon addition of AgOTf, a precipitate immediately formed. The solution was filtered through a fine porosity frit, and the green filtrate was refluxed for approximately 30 min. The volatiles were removed under reduced pressure, and the product was recrystallized by layering a methylene chloride solution with hexanes. Yellow crystals (0.0728 g, 49%) were collected after drying. CV (DMA, TBAH, 100 mV/s): $E_{1/2} = -0.65$ V (II/I) (quasi-reversible); $E_{p,a} = 0.87$ V. Anal. Calcd for $C_{14}H_{19}BF_3N_6O_4PReS$: C, 25.78; H, 2.94; N, 12.88. Found: C, 25.92; H, 3.14; N, 13.15.

TpRe(CO)(PMe$_3$)(η^2-naphthalene) (12). To a DME solution (approximately 20 mL) of TpRe(CO)(PMe$_3$)(η^2-cyclohexene) (**7**) (0.4064 g, 0.694 mmol) was added AgOTf (0.1784 g, 0.694 mmol, dissolved in 8 mL of DME). Upon addition of the AgOTf, a precipitate immediately formed. The resulting slurry was stirred for 10 min, and then ferrocene (0. 0286 g, 0.154 mmol, 0.22 equiv based on **7**, dissolved in 2 mL of DME) was added. After 15 min of stirring, the solution was vacuum filtered through a fine porosity frit. The volume of the green filtrate was reduced to approximately 15 mL in vacuo, and 30 mL of hexanes was added in order to precipitate the metal complex. The precipitate was separated from the solution via vacuum filtration through a medium porosity frit, and the filtrate was discarded. Next, the green solid was extracted with DME (30 mL), and the filtrate was refluxed for 15 min. After cooling the solution to room temperature, 0.5143 g of naphthalene (4.01 mmol, 5.8 equiv) followed by 0.4662 g of sodium mercury amalgam (5%, 1.01 mmol, 1.5 equiv) were added. The solution was stirred for 1.5 h, during which time a precipitate formed and elemental mercury could be observed. The resulting brownish-orange solution was filtered, and the volatiles were removed from the filtrate under a dinitrogen purge. The oil was purified via column chromatography on deactivated alumina utilizing approximately 5:1 hexanes/toluene (approximately 250 mL used and discarded) followed by 2:1 diethyl ether/hexanes as eluent (approximately 250 mL of eluent collected). Solvent evaporation yielded a pale yellow solid, which was washed with approximately 10 mL of 4:1 hexanes/diethyl ether (0.2429 g, 55% yield). IR (KBr): $\nu_{CO} = 1825$ cm^{-1}; $\nu_{BH} = 2472$ cm^{-1}. ^{1}H NMR (acetone-d_6, δ) (for numbering scheme see below): 7.94, 7.83, 7.79, 7.78, 7.45, 6.82 (each 1H, d, Tp C*H*, 3 and 5 position), 6.35, 6.15, 6.09 (each 1H, t, Tp C*H*, 4 position), 7.25 (1H, dd, $^3J_{HH} = 7$ Hz, $^4J_{HH} = 2$ Hz, unbound naphthalene C(5) proton), 7.18 (1H, ddd, $^3J_{HH} = 5, 9$ Hz, $^4J_{HH} = 2$ Hz, unbound naphthalene C(3) proton), 7.03−7.02 (2H, m, overlapping ddd for naphthalene C(6) and C(7) protons), 6.70 (1H, dd, $^3J_{HH} = 7$ Hz, $^4J_{HH} = 2$ Hz, unbound naphthalene C(8) proton), 6.34 (1H, d (br), $^3J_{HH} = 9$ Hz, unbound naphthalene C(4) proton), 4.26 (1H, ddd, $^3J_{HH} = 8, 5$ Hz, $^3J_{PH} = 13$ Hz, bound naphthalene C(2) proton), 3.04 (1H, dt, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 2$ Hz, $^3J_{PH} = 2$ Hz, bound naphthalene C(1) proton), 1.38 (9H, d, $^2J_{PH} = 8$ Hz, P(CH_3)$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 196.2 (d, $^2J_{PC} = 7$ Hz, *C*O), 146.9, 144.0, 139.0, 136.1, 135.8, 135.7 (each a d of t, $^1J_{CH} = 180-188$ Hz, $J_{CH} = 8$ Hz, Tp *C*H, 3 and 5 position), 106.0, 104.7(2:1 ratio, each a d of t, $^1J_{CH} = 180$ Hz, $^2J_{CH} = 8$ Hz, Tp *C*H, 4 position), 144.1, 130.6 {unbound naphthalene carbons, ring juncture carbons C(9) and C(10)}, 135.8 (isochronous with Tp carbon), 129.7, 125.9, 124.0, 123.8, 120.1 (each a d, $^1J_{CH} = 155-160$ Hz, unbound naphthalene carbons), 57.4 (d, $^1J_{CH} = 154$ Hz, bound naphthalene carbon), 53.1 (dd, $^1J_{CH} = 160$ Hz, $^2J_{PC} = 7$ Hz, bound naphthalene carbon), 15.8 (qd, $^1J_{CH} = 126$ Hz, $^1J_{PC} = 31$ Hz, P(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, δ): -23.4 (*P*Me$_3$). CV (DMA, TBAH, 100 mV/s): $E_{1/2}$ (quasi-reversible) = 0.19 V (II/I). Anal. Calcd for $C_{23}H_{27}BN_6OPRe$: C, 43.75; H, 4.31; N, 13.31. Found: C, 43.39; H, 4.75; N, 13.79.

TpRe(CO)(PMe$_3$)(η^2-phenanthrene) (13). TpRe(CO)(PMe$_3$)(OTf) (**10**) was prepared similar to the procedure for complex **12** using 0.3939 g of TpRe(CO)(PMe$_3$)(η^2-cyclohexene) (**7**) (0.673 mmol), 0.1747 g of AgOTf (0.680 mmol, 1.01 equiv), and 0.0261 g of ferrocene (0.140 mmol, 0.21 equiv based on **7**). The solution was cooled to room temperature, and phenanthrene was added (1.2835 g, 7.20 mmol, 107 equiv) followed by 0.3971 g of sodium mercury amalgam (5%, 0.864 mmol, 1.3 equiv). The solution was stirred for 2.5 h, during which time a bright yellow-green precipitate formed and elemental mercury could be observed. The resulting solution was filtered, and the yellow-green solid was dried in vacuo. Analytically pure **13** was isolated in 27% yield (0.1254 g). IR (KBr): $\nu_{CO} = 1820$ cm^{-1}; $\nu_{BH} = 2471$ cm^{-1}. ^{1}H NMR (acetone-d_6, δ) (for numbering scheme see below): 7.97, 7.80, 7.75, 7.65, 7.58, 6.21 (each 1H, d, Tp C*H*, 3 and 5 position), 6.41, 6.10, 5.97 (each 1H, t, Tp C*H*, 4 position), 8.23 (1H, dd, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 1$ Hz, unbound phenanthrene C(5) proton), 8.21 (1H, dd, $^3J_{HH} = 7$ Hz, $^4J_{HH} = 1$ Hz, unbound phenanthrene C(4) proton), 7.73 (1H, m, overlap with Tp doublet, unbound phenanthrene C(1) proton), 7.26 (1H, ddd, $^3J_{HH} = 9$ and 8 Hz, $^4J_{HH} = 1$ Hz, unbound phenanthrene C(2) proton), 7.12 (2H, m, unbound phenanthrene C(3) and C(6) protons), 7.03 (1H, ddd, $^3J_{HH} = 8$ and 7 Hz, $^4J_{HH} = 1$ Hz, unbound phenanthrene C(7) proton), 6.44 (1H, dd, $^3J_{HH} = 8$ Hz, $^4J_{HH} = 1$ Hz, unbound phenanthrene C(8) proton), 5.08 (1H, dd, $^3J_{HH} = 8$ Hz, $^2J_{PH} = 14$ Hz, bound phenanthrene C(10) proton), 3.11 (1H, dd, $^3J_{HH} = 8$ Hz, $^3J_{PH} = 1$ Hz, bound phenanthrene C(9) proton), 1.30 (9H, d, $^2J_{PH} = 8$ Hz, P(C*H*$_3$)$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ): 196.8 (s, *C*O), 147.2, 145.5, 145.4, 144.5, 139.8, 136.4, 136.0, 135.9, 131.1, 130.5, 129.1, 127.3, 125.9, 125.1, 124.4, 124.3, 122.9, 122.0 (resonances for 6 Tp carbons, 3 and 5 position, and 12 unbound phenanthrene carbons), 106.1, 106.0, 104.7 (each a s, Tp *C*H, 4 position), 58.0 (s, bound phenanthrene carbon), 51.4 (d, $^2J_{PC} = 8$ Hz, bound phenanthrene carbon), 16.3 (d, $^1J_{PC} = 31$ Hz, P(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (acetone-d_6, δ): -19.5 (*P*Me$_3$). CV (DMA, TBAH, 100 mV/s): $E_{1/2}$ (quasi-reversible) = 0.17 V (II/I). Anal. Calcd for $C_{27}H_{29}BN_6OPRe$: C, 47.58; H, 4.29; N, 12.33. Found: C, 47.40; H, 4.43; N, 12.26.

TpRe(CO)(PMe$_3$)(η^2-furan) (14). TpRe(CO)(PMe$_3$)(OTf) (**10**) was prepared similar to the procedure for complex **12** using 0.4481 g of TpRe(CO)(PMe$_3$)(η^2-cyclohexene) (**7**) (0.765 mmol), 0.1967 g of AgOTf (0.765 mmol), and 0.0361 g of ferrocene (0.194 mmol, 0.25 equiv). After cooling the solution to room temperature, 1.1 mL of furan (15.3 mmol, 20 equiv) followed by 0.5323 g of sodium mercury amalgam (5%, 1.16 mmol, 1.5 equiv) were added. The solution was stirred for 2 h, during which time a precipitate formed and elemental mercury could be observed. The resulting brown solution was filtered through a fine porosity frit, and the volatiles were removed from the filtrate under reduced pressure. The oil was purified via column chromatography on deactivated alumina with 2:1 diethyl ether/hexanes as eluent (approximately 250 mL of eluent collected). Solvent evaporation yielded a pale yellow solid (0.3550 g, 81% yield). IR (KBr): $\nu_{CO} = 1826$ cm^{-1}; $\nu_{BH} = 2478$ cm^{-1}. ^{1}H NMR (acetone-d_6, δ): Two isomers were observed in a 2.1:1.0 ratio. Major isomer: 8.47, 7.94, 7.36 (each 1H, d, Tp C*H*), 7.83, 7.80 (each 1.5H, d, Tp C*H*, isochronous with Tp CH of minor isomer), 7.36 (1H, d, Tp C*H*, overlap with Tp CH of minor isomer), 6.31−6.19 (overlapping Tp t's for major and minor isomers), 6.49 (1H, $^3J_{HH} = 2$ Hz, unbound α-proton), 5.94 (2H, overlap of furan unbound β-proton and furan bound α-proton, unbound proton is a t, $^3J_{HH} = 2$ Hz, bound proton is a dd, $^3J_{HH} = 4$ Hz and $^3J_{PH} = 2$ Hz), 4.47 (1H, ddd, $^3J_{HH} = 4$, 2 Hz, $^3J_{PH} = 11$ Hz, bound β-proton); minor isomer: 8.32, 7.91 (each 1H, d, Tp C*H*), 7.83, 7.80 (each 1.5 H, d, Tp C*H*, isochronous with Tp CH of major isomer), 7.71 (1H, d, Tp C*H*), 7.37 (1H, d, Tp C*H*, overlap with major resonance), 7.29 (1H, dd, $^3J_{HH} = 4$ Hz, $^3J_{PH} = 16$ Hz, bound α-proton), 6.50 (1H, d, $^3J_{HH} = 2$ Hz, unbound α-proton), 6.32 (1H, t, $^3J_{HH} = 2$ Hz, unbound β-proton), 2.98 (1H, ddd, $^3J_{HH} = 4$, 2 Hz, $^3J_{PH} = 2$ Hz, bound β-proton). ^{13}C NMR (CD$_2$Cl$_2$, δ) (major diastereomer): 198.2 (d, $^2J_{PC} = 7$ Hz, *C*O (each a d of t, $^1J_{CH} = 182{-}188$ Hz, $J_{CH} = 8$ Hz, Tp *C*H, 3 and 5 position), 147.7, 143.5, 143.4, 141.4, 140.4, 140.2, 136.1, 135.9, 135.8, 135.7, 134.7, 113.7 (dd, $^1J_{CH} = 171$ Hz, $^3J_{CH} = 13$ Hz, unbound furan β-carbon), 106.2, 105.9, 105.6 (each a d of t, $^1J_{CH} = 177$ Hz, $^2J_{CH} = 8$ Hz, Tp *C*H, 4 position), 102.5 (d (br), $^1J_{CH} = 181$ Hz, unbound furan α-carbon), 48.9 (dt, $^1J_{CH} = 166$ Hz, $^2J_{PC} = 10$ Hz, $^3J_{CH} = 10$ Hz, bound furan β-carbon), 17.0 (qd, $^1J_{CH} = 127$ Hz, $^1J_{PC} = 32$ Hz, P(*C*H$_3$)$_3$). ^{13}C NMR (CD$_2$Cl$_2$, δ) (minor diastereomer, only chemical shifts reported, splitting patterns and coupling constants are similar to major diastereomer): 198.3 (*C*O), 147.7, 143.5, 143.3, 141.4, 140.4, 140.2, 136.1, 135.9, 135.8, 135.7, 134.7, 114.6 (unbound furan β-carbon), 99.2 (bound furan α-carbon), 106.1, 105.7 (Tp *C*H, 4 position, only two resonances located; other two resonances are likely isochronous with major diastereomer resonances), 99.2 (bound furan α-carbon) 51.6 (bound furan β-carbon),16.8 (P(*C*H$_3$)$_3$). ^{31}P{^{1}H} NMR (acetone-d_6, δ): -19.6 (*P*Me$_3$ of minor diastereomer), -21.3 (*P*Me$_3$ of major diastereomer). CV (DMA, TBAH, 100 mV/s): $E_{p,a} = 0.30$ V (II/I). Anal. Calcd for $C_{17}H_{23}BN_6O_2PRe$: C, 35.73; H, 4.06; N, 14.71. Found: C, 35.30; H, 4.42; N, 14.64.

TpRe(CO)(PMe$_3$)(thiophene) (15). TpRe(CO)(PMe$_3$)(OTf) (**10**) was prepared similar to the procedure for complex **12** using 0.4268 g of TpRe(CO)(PMe$_3$)(η^2-cyclohexene) (**7**) (0.729 mmol), 0.1887 g of AgOTf (0.734 mmol, 1.01 equiv), and 0.0272 g of ferrocene (0.146 mmol, 0.2 equiv based on **7**). The solution was cooled to room temperature, and 1.2 mL of thiophene (14.6 mmol, 20 equiv based on **7**) followed by 0.4380 g of sodium mercury amalgam (5%, 0.953 mmol, 1.3 equiv based on **7**) were added. The solution was stirred for 4 h, during which time a precipitate formed and elemental mercury could be observed. The solution was filtered through a fine porosity frit, and the volatiles were removed from the filtrate under reduced pressure. The oil was purified via column chromatography on deactivated alumina with 5:1 diethyl ether/hexanes as eluent. Solvent removal from the eluent (approximately 250 mL collected) yielded a honey yellow solid (0.3292 g, 77% yield). IR (KBr): $\nu_{CO} = 1826$ cm^{-1}; $\nu_{BH} = 2478$ cm^{-1}. ^{1}H NMR (acetone-d_6, δ): Three isomers were observed in a 3.2:2.0:1.0 ratio. 8.68 (d, major isomer, Tp C*H*), 8.30 (d, middle isomer, Tp C*H*), 7.90−7.70 (several overlapping Tp d), 6.28 to 6.15 (several overlapping Tp t's). Minor isomer (η^1-bound): 7.43 (2H, m, thiophene α proton overlap with Tp d), 7.13 (12H, m, thiophene β proton). Major isomer (η^2-bound): 6.67 (1H, dd, $^3J_{HH} = 5$ Hz, $^4J_{HH} = 2$ Hz, unbound β-proton), 6.09 (1H, dd, $^3J_{HH} = 5$ Hz, $^3J_{HH} = 1$ Hz, unbound α-proton), 4.63 (1H, ddd, $^3J_{PH} = 13$ Hz, $^3J_{HH} = 7$ Hz, $^4J_{HH} = 1$ Hz, bound β-proton), 3.81 (1H, ddd, $^3J_{PH} = 2$ Hz, $^3J_{HH} = 7$ Hz, $^3J_{HH} = 2$ Hz, bound α-proton). Minor η^2-diastereomer: 6.87 (1H, dd, $^3J_{HH} = 5$ Hz, $^4J_{HH} = 2$ Hz, unbound α-proton), 6.13 (1H, dd, $^3J_{HH} = 5$ Hz, $^3J_{HH} = 2$ Hz, unbound β-proton), 5.30 (1H, ddd, $^3J_{PH} = 13$ Hz, $^3J_{HH} = 7$ Hz, $^3J_{HH} = 1$ Hz, bound α-proton), 3.23 (1H, dt, $^3J_{PH} = 2$ Hz, $^3J_{HH} = 7$ Hz, $^4J_{HH} = 2$ Hz, bound β-proton). ^{13}C NMR (CD$_2$Cl$_2$, δ) (data reported for major diastereomer only): 197.6 (d, $^2J_{PC} = 8$ Hz, *C*O), 147.2, 140.0, 139.6, 136.2, 135.9, 135.3 (Tp *C*H, 3 and 5 position), 106.3, 105.9, 105.5 (Tp *C*H, 4 position), 131.7 (unbound thiophene α-carbon), 119.2 (unbound thiophene β-carbon), 65.0 (bound thiophene α-carbon), 61.0 (d, $^2J_{PC} = 10$ Hz, bound thiophene β-carbon), 16.7 (d, $^1J_{PC} = 32$ Hz, P(*C*H$_3$)$_3$). ^{31}P{^{1}H} (acetone-d_6, δ): -22.0 (major η^2 diastereomer), -20.2 (minor η^2 diastereomer), -25.3 (η^1 isomer) (ratio of 3.2:2.0:1.0). CV (DMA, TBAH, 100 mV/s): $E_{1/2} = 0.01$ V (II/I; quasi-reversible). Anal. Calcd for $C_{17}H_{23}BN_6OPReS \cdot 1/9Et_2O$ (Note: 1/9 mol of diethyl ether was observed in the ^{1}H NMR of the analysis sample): C, 35.17; H, 4.08; N, 14.11. Found: C, 35.43; H, 4.35; N, 14.54.

TpRe(CO)(PMe3)(η^2-acetone) (17). TpRe(CO)(PMe$_3$)(OTf) (**10**) was prepared similar to the procedure for complex **12** using 0.2501 g of TpRe(CO)(PMe$_3$)(η^2-cyclohexene) (**7**) (0.427 mmol), 0.1097 g of AgOTf (0.427 mmol), and 0.0266 g of ferrocene (0.143 mmol, 0.33 equiv). After cooling the solution to room temperature, 5.0 mL of acetone (68.1 mmol, 159 equiv) followed by 0.4339 g of sodium mercury amalgam (5%, 0.944 mmol, 2.2 equiv) were added. The solution was stirred for 2 h, during which time a precipitate formed and elemental mercury could be observed. The resulting yellow solution was filtered through a fine porosity frit, and the volatiles were removed from the filtrate under reduced pressure. The product was purified via column chromatography on deactivated alumina with 2:1 diethyl ether/hexanes as eluent (approximately 200 mL of eluent collected) (0.1862 g, 78% yield). IR (KBr): $\nu_{CO} = 1819$ cm^{-1}; $\nu_{BH} = 2482$ cm^{-1}. ^{1}H NMR (acetone-d_6, δ): 8.19, 8.12, 7.85, 7.81, 7.76, 7.68 (each 1H, d, Tp C*H* 3 and 5 position), 6.25, 6.23, 6.22 (each 1H, t, Tp C*H* 4 position), 2.25 (3H, s, acetone CH_3), 1.41 (9H, d, $^2J_{PH} = 9$ Hz, P(CH_3)$_3$), 0.98 (3H, s, acetone CH_3). ^{13}C NMR (acetone-d_6, δ): 200.4 (d, $^2J_{PC} = 10$ Hz, *C*O), 149.1, 144.3, 142.5, 136.7, 135.7 (1:1:1:1:2, each a dt, $^1J_{CH} = 186-187$ Hz, $J_{CH} = 7$ Hz, Tp *C*H 3 and 5 position), 106.9, 106.5, 105.4 (each a dt, $^1J_{CH} = 176-179$ Hz, $^2J_{CH} = 7$ Hz, Tp CH 4 position), 84.2 (acetone carbonyl carbon), 33.4 (q, $^1J_{CH} = 123$ Hz, acetone CH$_3$), 25.6 (q, $^1J_{CH} = 123$ Hz, acetone CH$_3$), 14.3 (qd, $^1J_{CH} = 128$ Hz, $^1J_{PC} = 32$ Hz, P(CH$_3$)$_3$). ^{31}P{^{1}H} NMR (acetone-d_6, δ): −11.9 (*P*Me$_3$). CV (DMA, TBAH, 50 mV/s): $E_{p,a} = 0.26$ V (II/I). Anal. Calcd for $C_{16}H_{25}BN_6O_2PRe$: C, 34.23; H, 4.49; N, 14.97. Found: C, 34.05; H, 4.50; N, 15.05.

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Supporting Information Available: Synthetic procedures and full characterization data for complexes; details of the X-ray diffraction study, a labeled ORTEP diagram, crystal and refinement data, bond lengths and angles, atomic coordinates and anisotropic displacement parameters. This material is available free of charge via the Internet at http://pubs.acs.org.

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